

Ginzburg Number of a Homopolymer–Diblock Copolymer Mixture Covering the 3D-Ising, Isotropic Lifshitz, and Brasovskii Classes of Critical Universality

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(Received 6 August 2004; published 21 March 2005)

The Ginzburg number Gi of deuterated poly(butadiene) (dPB) and poly(styrene) (PS) homopolymer blend of critical composition mixed with a dPB-PS symmetric diblock copolymer was determined from small angle neutron scattering. A 3 orders of magnitude change of Gi was determined between binary polymer blend and diblock copolymer melt. The strongest change of Gi is observed within the isotropic Lifshitz regime of critical universality occurring over a 3% range of diblock concentration and interpolates the corresponding Gi of the 3D-Ising and Brasovskii regimes. A Lifshitz critical point was not observed consistent with the proposed lower critical dimension $d_{LCP} = 4$.

DOI: 10.1103/PhysRevLett.94.117801

PACS numbers: 61.25.Hq, 61.12.Ex, 64.60.Cn, 64.60.Fr

The Ginzburg number, $Gi := (T_X - T_C)/T_C$, is defined as a reduced temperature of T_X which determines the range of strong thermal fluctuations around the critical point (T_C , critical temperature) where nonlinear effects lead to a class of critical universality different from mean field [1–5]. We present here Gi of a three component polymer melt of a binary A/B homopolymer blend of critical composition and a symmetric $A-B$ diblock copolymer which was determined by small angle neutron scattering (SANS) experiments. Such systems show a complex phase diagram as they bridge the 3D-Ising, isotropic Lifshitz, and Brasovskii classes of critical universality. In 3D-Ising systems the unstable fluctuation modes approach infinite length while in Brasovskii systems fluctuations are stronger and their unstable modes are of finite length [2]. Such characteristic differences can be visualized from the Ginzburg number which follows a $Gi \propto 1/N$, $\propto 1/N^{(2/5)}$, and $\propto 1/N^{(1/3)}$ (N degree of polymerization) scaling for an ordinary critical point in A/B polymer blends, a Lifshitz critical point (LCP) in $A/B/A-B$ mixtures, and an order-disorder transition in $A-B$ diblock copolymers, respectively [6–8]. Isotropic LCP behavior is described by the Hamiltonian

$$H = \frac{1}{2} \int d^3x \{ c_2 (\nabla \Phi)^2 + c_4 (\nabla^2 \Phi)^2 + r \Phi^2 + u \Phi^4 + u_6 \Phi^6 \} \quad (1)$$

and represents an expansion with respect to the scalar order parameter $\Phi(x)$ which for incompressible systems is defined as the volume fraction of one of the two monomer components [3]. The addition of diblock copolymers gives rise to a reduction of surface energy and thereby to a reduction of the parameter c_2 . This parameter is positive at low copolymer content; it is zero at the composition of the Lifshitz line (LL) and at the LCP, and becomes negative for larger diblock content. In the case of a positive c_2 one has the characteristics of polymer blends with the inverse susceptibility $r = 0$ at the critical point, while both, $r = 0$ and $c_2 = 0$, have to be fulfilled at the LCP. For higher diblock concentration one gets $c_2 < 0$ and $u < 0$, which

are the conditions of a first order phase transition. The two terms $c_4 (\nabla^2 \Phi)^2$ and $u_6 \Phi^6$ are necessarily positive for stability reasons. LCP universality is found in many systems as magnetic systems [5,9], ferroelectric liquid crystals [10], liquid crystals [11], polyelectrolytes [12], random block copolymers [13], and oil/water/surfactant microemulsions [14]. It is the common feature of those systems that the ordered phase changes from a spatially uniform (two-phase) to a spatially modulated (lamella) structure in dependence of an external field which is represented here by the diblock copolymer. The ordered and disordered phases meet at the LCP. This scenario, however, is valid only within mean field approximation. Thermal composition fluctuations lead to a more complex phase diagram as was demonstrated in several SANS experiments and by Monte Carlo simulations; the isotropic LCP is suppressed and both ordered phases are separated by a microemulsion phase [15–20]. On the other hand, the corresponding critical exponents of the susceptibility and correlation length could be determined within the LCP regime [18,19]. The formation of a microemulsion phase is plausible from theoretical considerations as was recently reviewed in [21]; the isotropic LCP has the lower critical dimension of $d_{LCP} = 4$, which means that long range order is destroyed by thermal fluctuations in ordinary systems. Another argument in the same direction is the different strength of fluctuations expressed by Gi in 3D-Ising and Brasovskii regimes [7]. The principal result of this Letter is Gi in Fig. 4, shown below; it shows an overall difference of 3 orders of magnitude in 3D-Ising and Brasovskii classes of critical universalities. Remarkably, a 1 to 2 orders of magnitude different Gi is interpolated within the LCP regime covering a 3% copolymer interval. In the following we introduce the scattering laws and susceptibilities from which Gi was determined and then discuss the experimental findings.

The phase diagram of the present system is depicted in Fig. 1. A more detailed discussion of this phase diagram is given in [19] while phase diagrams of other $A/B/A-B$

mixtures are presented in [15–18]. The polymers are poly(styrene) (PS) and deuterated poly(butadiene) (dPB). The deuteration of PB was necessary in order to achieve good neutron scattering contrast and to measure the fluctuations between the PS and dPB monomers; irrespectively, they are part of the homopolymer or copolymer. The molar volume was $V_{\text{dPB}} = 2720$, $V_{\text{PS}} = 2180$, and $V_{\text{dPB-PS}} = 15\,400$ always in units of cm^3/mol . The polymers were synthesized in our laboratory; their synthesis and characterization have been described elsewhere [22]. The homopolymers were always mixed in portions of their critical composition ($\Phi_{\text{PB}} = 0.42$). Their molar volume had to be chosen relatively small for a $T_C \approx 100^\circ\text{C}$ while the diblock copolymer was roughly 6 times larger in order to achieve an ordering temperature in the same range ($T_{\text{ODT}} = 69.4^\circ\text{C}$). The LL divides the disordered phases into a “homopolymer” and a “diblock copolymer” part. Another Lifshitz line separates the ordered phases; within the blend rich part one has a two-phase regime of large domains and a droplet microemulsion phase, while within the diblock rich part are a bicontinuous microemulsion and lamellar phase. The neutron experiments were performed at the SANS diffractometer KWS1 at the FRJ-2 reactor in Jülich. The correction and calibration of the data were standard procedure [23].

Disordered phases become heterogeneous on a mesoscopic length scale by thermal composition fluctuations. This length is described by the correlation length ξ which, according to $\xi = \xi_0 \tau^{-\nu}$, scales with the reduced temperature $\tau = (T - T_C)/T$ and the critical exponent ν ; at the critical point ξ becomes infinite. The structure factor $S(Q)$ is determined from scattering experiments and measures

thermal composition fluctuations as a function of the momentum transfer Q which is defined as $Q = (4\pi/\lambda) \times \sin(\delta/2)$ from neutron wavelength λ and scattering angle δ . $S(Q)$ looks different on both sides of the LL as shown in Fig. 2. Within the homopolymer part the structure factor $S(Q)$ is described according to

$$S(Q) = S(0)/[1 + (\xi Q)^2 + (\eta Q)^4] \quad (2)$$

with the correlation length $\xi = \sqrt{l_2 S(0)}$ and $\eta = \sqrt[4]{l_4 S(0)}$ (l_2 and l_4 proportional to c_2 and c_4 in the Hamiltonian, respectively) [6]. The maximum of $S(Q)$ is observed at $Q = 0$; it represents a susceptibility $S(0) \equiv r^{-1}$ in accordance with Eq. (1) and follows the scaling law $S(0) = C\tau^{-\gamma}$ within mean field, 3D-Ising, and LCP regimes (with C the critical amplitude and γ the critical exponent). Within the Ising regime η can be neglected and Eq. (2) becomes the Ornstein-Zernike law. The crossover of $S(0)$ from the mean field to the Ising regime is described in Eq. (3); the reduced temperature $\hat{\tau} = \tau/\text{Gi}$ is an explicit

$$\hat{\tau} = (1 + 2.333\hat{S}(0)^{\Delta/\gamma})^{(\gamma-1)/\Delta} \times [\hat{S}^{-1}(0) + (1 + 2.333\hat{S}(0)^{\Delta/\gamma})^{-\gamma/\Delta}] \quad (3)$$

function of the rescaled susceptibility $\hat{S}(0) = S(0)\text{Gi}/C_{\text{MF}}$, with the Ising critical exponents $\gamma = 1.24$ and $\Delta = 0.5$, and the mean field critical amplitude C_{MF} [24]. This universal expression is a good description of thermal fluctuations in polymer blends [4]. As c_2 becomes zero at LL, the next higher order term η in Eq. (2) becomes relevant and overtakes the part of the correlation length. As a result, the mean field critical exponent becomes $\nu = 0.25$, which is

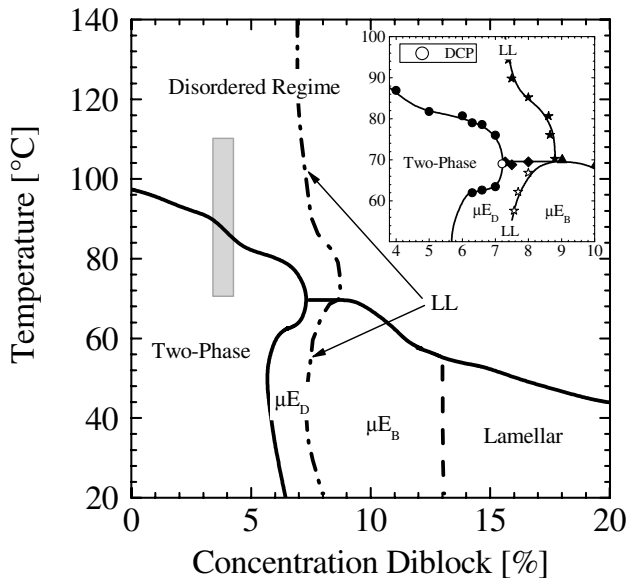


FIG. 1. Temperature-diblock concentration plane of the phase diagram of the three component blend PS/dPB/PS-dPB of fixed critical blend composition. The inset depicts the Lifshitz critical region in more detail.

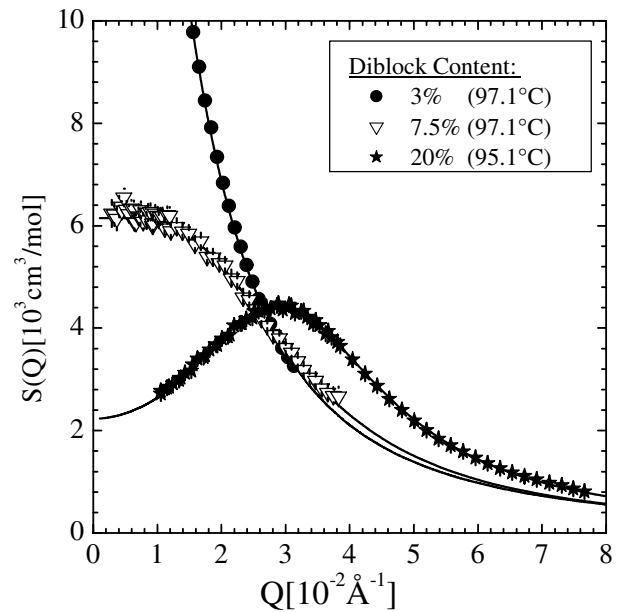


FIG. 2. Structure factor measured around 96°C in the disordered regime above the two-phase, microemulsion, and lamellar ordered regimes.

half of the ordinary one. Another aspect of diminishing surface energy is related to its role as the restoring force for thermal fluctuations [6–8].

Within the “diblock” regime the structure factor $S(Q)$ can be approximately described according to

$$S^{-1}(Q) = a/(b + Q^2) + c + dQ^2. \quad (4)$$

The parameters a to d deliver the relevant information as the maximum of $S(Q)$ at Q^* representing a susceptibility (Fig. 2). Kielhorn *et al.* have chosen this expression in order to consider the effects of thermal fluctuations by evaluating the corresponding renormalized parameters [7]. Within the disordered phase the susceptibility in Eq. (5),

$$S^{-1}(Q^*) = 2[\Gamma_C V - \Gamma_{\text{ren}} V]/V, \quad (5)$$

is described by the renormalized Flory-Huggins (FH) parameter Γ_{ren} and the FH parameter Γ_C at the critical temperature [8]. The FH parameter is expressed according to $\Gamma = \Gamma_h/T - \Gamma_\sigma$ with the enthalpic (Γ_h) and entropic (Γ_σ) terms. Susceptibilities measured within the three universality regimes are plotted in Fig. 3. The sample with 3% copolymer content is still within the 3D-Ising regime as $S(0)$ is described by the crossover function [Eq. (3)] as depicted by the solid line. At 7.5% diblock

content the LL is passed 2 times; at high and low temperatures the susceptibility is described by $S(Q^*)$ (solid symbols) and at intermediate temperature by $S(0)$ (open symbols). The solid line represents a fit of Eq. (5). The deviation below 69.6 °C indicates the transition to the droplet microemulsion phase [19] and represents the maximal $S(0)$ and ξ along this path. The isothermal line between double critical point (DCP) and LL [indicated by rhombs (◆) in the inset of Fig. 1] represents the critical path of the scaling field $\varphi = (\Phi - \Phi_{\text{DCP}})/\Phi$ with the critical exponent $\gamma = (1.55 \pm 0.15)$ according to $S^{-1}(0) \propto \varphi^\gamma$. The other path at $\Phi = \Phi_{\text{DCP}}$ leads to a twice as large γ according to $S^{-1}(0) \propto \tau^{2\gamma}$ and $\tau = (T - T_{\text{DCP}})/T$ [25,26]. The 20% sample is within the Brasovskii regime; it is described by the susceptibility $S(Q^*)$ and shows an ordering transition which became visible by a second order peak not shown here.

The Ginzburg criterion for 3D-Ising systems [Eq. (6)] is determined by the ratio

$$Gi := 0.069(C_+/C_{\text{MF}})^{1/(\gamma-1)} \quad (6)$$

of the mean field and 3D-Ising critical amplitudes C and the 3D-Ising critical exponent γ [27]. In case of incompressible blends ($\Gamma_\sigma = 0$) this expression leads to the well known $Gi \propto 1/V$ [1,2]. Another expression $Gi := (T_C^{\text{MF}} - T_C)/T_C$ is obtained from extrapolation of the crossover function [Eq. (3)] into the classical regime with the crossover temperature identical with the mean field critical temperature ($T_X = T_C^{\text{MF}}$) (Eqs. 3.6 and 3.7 in [3]). The Ginzburg number of the LCP and Brasovskii regimes is identified as \tilde{Gi} in Eq. (7) and describes the fluctuation part of the renormalized

$$\Gamma_{\text{ren}} V = \Gamma V - \tilde{Gi} \times F_X \quad (7)$$

FH parameter. The corresponding parameters were determined by Kielhorn *et al.* [7] according to $\tilde{Gi} \propto 1/\sqrt{N}$ and F_X (Eqs. 3.13 and 3.20 in [7]; Eqs. 9 and 12 in [18]). So, F_X was evaluated from the parameters of $S(Q)$ [Eq. (4)], and the two parameters Γ and \tilde{Gi} are adjustable parameters.

All experimental Gi values are depicted in Fig. 4. Gi of the binary homopolymer blend and diblock copolymer is different by 3 orders of magnitude and tentatively shows a $Gi \propto \Phi^\alpha$ scaling with, respectively, α equal to 7.7 and 0.5 in the isotropic Lifshitz and Brasovskii regimes. A critical analysis of these results, however, has to consider that Gi from Ising and the two other regimes were derived from different theories and most probably there exists an unknown factor between them. An evaluation of Gi from $Gi := (T_C^{\text{MF}} - T_C)/T_C$ might be a proper cross-check; in the Ising regime we got the same Gi as it is clear from its definition above, while for the LC and Brasovskii regimes we derived the same shape but an order of magnitude smaller Gi . In the latter two regimes Gi was slightly underestimated as T_C could not be determined and T_{ODT} was chosen instead. So, our experiments give clear evidence of

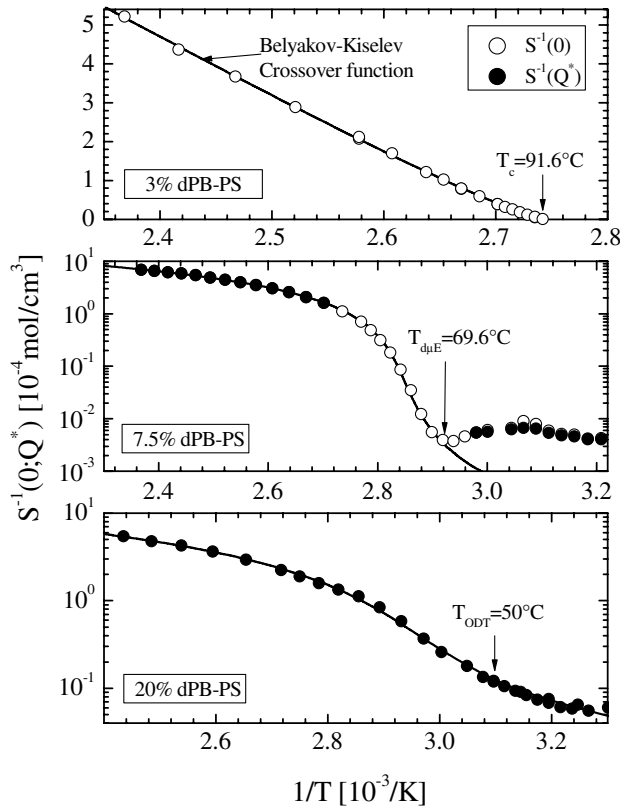


FIG. 3. Susceptibility versus inverse temperature for three diblock concentrations. The empty and full dots represent $S(0)$ and $S(Q^*)$, respectively.

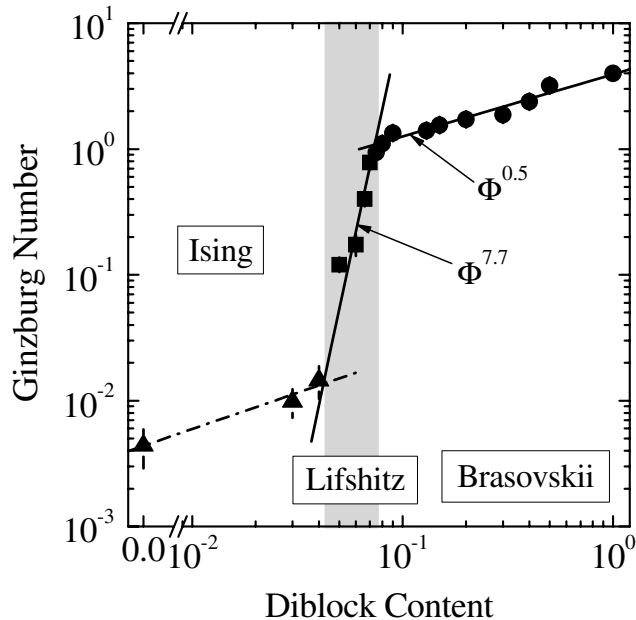


FIG. 4. Ginzburg number versus diblock concentration. The different symbols represent G_i within the different universality classes and the crossover between them as indicated.

the very different strengths of thermal fluctuations within the 3D-Ising, isotropic Lifshitz, and Brasovskii classes of critical universality.

The Ginzburg number of an $A/B/A-B$ polymer blend was evaluated from the SANS susceptibility by applying theoretical concepts of 3D-Ising crossover function [Eq. (3)] and of LCP and Brasovskii classes of critical universality [Eq. (7)]. G_i in Brasovskii and 3D-Ising regimes differs by 2 to 3 orders of magnitude and is smoothly interpolated over a 3% diblock interval in the LCP regime. The center of this crossover is at 6% diblock content and ends at 7.5% which is near the double critical point (DCP) [19]. Such a strong change of G_i is understood from a decrease of the surface energy expressed by the coefficient c_2 in the Hamiltonian [Eq. (1)]. As soon as c_2 becomes negative (zero at LL), G_i shows a much smaller power law exponent.

An important difference between Ising and Brasovskii universality is demonstrated by the very different degree of thermal composition fluctuations. The LCP itself does not exist in this system as critical line and LL never cross. The nearest approach of both lines is the 1.3% diblock interval above the droplet microemulsion phase between DCP and LL. This result is consistent with the above mentioned lower critical dimension $d_{LCP} = 4$ which does not permit a LCP in ordinary systems [21]. So in ordinary dimension the LCP seems to be a realistic concept within the mean field approach only when fluctuations are irrelevant.

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